QUALITY ASSURANCE MANAGEMENT PROGRAMME FOR THE LIMNOLOGY UNIT DORSET RESEARCH CENTRE

B. A. Locke

DATA REPORT DR 85/4

DATA REPORT SERIES

The data presented in this report was collected by staff of the Water Resources Branch of the Ontario Ministry of the Environment as part of the Lakeshore Capacity Study or the Acid Precipitation in Ontario Study. This unreviewed report does not necessarily reflect the views or opinions of the Ontario Ministry of the Environment.

Quality Assurance Management Program for the Limnology Unit Dorset Research Centre

B. A. Locke

Limnology Section
Water Resources Branch

Ontario Ministry of the Environment
P.O. Box 39
Dorset, Ontario
POA 1E0

Data Report DR 85/4

PREFACE

The unpublished Data Report Series is intended as a readily available source of basic data collected for lakes and watersheds in the Muskoka-Haliburton area of Ontario. These data were collected as part of the Lakeshore Capacity Study and/or the Acid Precipitation in Ontario Study.

The limnological portion of the Lakeshore Capacity Study (1975-81) was inititated to investigate the relationships between lakeshore development and lake trophic status in low ionic strength Precambrian lakes. The Acid Precipitation in Ontario Study (1979-present) was initiated, in part, to investigate the effects of the deposition of strong acids on aquatic and terrestrial ecosystems in Ontario. The primary findings of these studies have been and will continue to be published as reviewed papers and technical reports.

ABSTRACT

The quality control/quality assurance programme that has been implemented since 1975 as part of the Lakeshore Capacity Study and continued with the Acidic Precipitation in Ontario Study, is outlined in this report. The objectives, organization and responsibility as well as the experimental procedures are described in detail. Presentation and evaluation of quality control data will be published in a separate report.

Locke, B.A. 1985. Quality Assurance Management Program for the Limnology Unit, Dorset Research Centre. Ont. Min. Envir. Data Report 85/4.

Table of Contents

1. Introduction

Environmental studies have been carried out at the Dorset Research Centre since the initiation of the Lakeshore Capacity Study in 1975. More recently, work has continued with the Acidic Precipitation in Ontario Study (1979 - present). Most of the research into the effects of acidic precipitation on aquatic ecosystems has been conducted at the Dorset Research Centre. In both programmes, study lakes and watersheds were selected with the intent of constructing mass balance models to predict changes in lake and stream chemistry and biota. Less intensively-studied lake systems were selected to test these models. Bulk precipitation collectors are also monitored throughout the study area. The locations of the principal study lakes, streams and precipitation collectors, and the field and laboratory methods used are outlined in Scheider *et al.* (1983a).

The quality control/quality assurance programme that has been implemented since 1975 as part of these studies is outlined in this report.

2. Quality Assurance Objectives

The primary objective of quality assurance is to ensure that the collection and reporting of data are complete, accurate, precise and representative. A supplementary objective is to isolate and quantify any or all sources of error or variation introduced to the procedure so that preventative measures can be taken to alleviate such problems.

There are four basic sources of variation inherent in our studies:

(i) spatial variability,

(ii) temporal variability

(both of which are real, and form the basis for many of the studies),

(iii) collection/handling variability, and

(iv) analytical variability.

The latter two may be assessed both collectively and individually in order to evaluate their contribution to the variability of the data.

In order to meet the primary objective several requirements must be fulfilled at all times. These requirements are standard for all scientific endeavours and were summarized in the form of an action plan in a recent internal report by Air Resources Branch staff (1984a). They are summarized below, with certain qualifiers for our specific needs.

(i) All sampling sites should meet acceptable siting criteria. Any deviations from these criteria should be documented and data collected from these sites closely scrutinized. All field sites are specified by a station identifier and samples should be obtained only from the designated sampling location. The sampling sites must be representative of naturally-occurring conditions.

(ii) Instrumentation, sample collection, sample handling, analysis and data reporting procedures must be well-defined. Documentation of these standard operating procedures, especially of changes to methodology, is updated periodically and is readily available to all personnel. Field procedures used before 1983 are described in Scheider *et al.* 1983a and an updated version (1983-85) will be available (Locke *et al.*, in prep.). Calibration and preventative maintenance on all equipment are carried out on a routine basis and records with this information are kept on file.

(iii) Standard operating procedures should be used by all personnel at all times. Personnel are thoroughly trained in using these procedures and estimates of variability as a function of personnel are evaluated through specialized QA sampling. Duties and responsibilities of all programme personnel are outlined to all individuals by field supervisors.

(iv) Estimates of accuracy and precision are established by the use of calibrations, blanks, standards, standard additions, spatial and temporal replicates, and other special studies that provide this information. The details of sampling methodology and sample container intercomparisons have also been addressed to isolate these as possible sources of variability. The results of these studies will be published separately (Locke et al., in prep.). Through the regular use of "blanks" the quality of sample containers and sampling equipment can be monitored continually.

(v) The quality of the data should be constantly scrutinized and reported on a regular basis. This report summarizes our efforts since 1975 to maintain the primary objectives as earlier stated; that is, providing data which are complete, accurate, precise and representative.

3. Organization and Responsibility

In 1975, an interministerial multidisciplinary study of the effects of recreational and urban development on lakes called the Lakeshore Capacity Study (LCS) was initiated. The Limnology Unit of the Water Resources Branch (WRB) conducted studies on the effects of development on water quality by means of detailed analysis of the hydrologic and nutrient budgets of the study lakes. During the course of that study (1975-1982), it was perceived that another problem, that of the effects of the depo-

sition of strong acids on aquatic and terrestrial ecosystems, also needed to be investigated. It became apparent that precipitation acidity was high while lake buffering capacities were low. Since lake acidification had been reported to result in undesirable changes in biotic communities, it was essential that the interaction of acid and nutrient-related effects be investigated. The QA/QC objectives that were established during the LCS have continued to be recognized throughout the Acidic Precipitation in Ontario Study (APIOS).

The routine sample types collected at the Dorset Research Centre that this report addresses fall into three broad categories: lakes, streams and precipitation. In each of the three categories a network of routine sampling stations has been selected based on specific criteria that are discussed more fully in section 4.

The Limnology Unit in Dorset is a part of the Aquatic Ecosystems Section that is based in Rexdale. The manager of the section is reponsible for administration of the study. The field programme is supervised from the headquarters located at the Dorset Research Centre. Project scientists, data managers, environmental technicians and some analytical chemists are located on site.

The Limnology Unit supervisor at Dorset is responsible for the implementation and co-ordination of the QA/QC plan for all facets of the research programme. Project scientists oversee all QA procedures that are employed in this plan. Environmental tech-

nicians are responsible for using accepted sampling methodologies, operation and maintenance of equipment and for fulfilling specific requirements for sample identification including site, operator, equipment used, performance, unusual occurrences during sampling period and maintenance of a logbook.

Chemical analyses of perishable parameters are carried out by the Laboratory Services Branch (LSB) of the Ministry of the Environment at Dorset. All other sample analyses are performed by the Water Quality Section (WQS) and Inorganic Trace Contaminants Section (ITC) of the LSB in Rexdale, Ontario.

The LSB has an internal quality assurance office that employs a rigorous QA/QC program for the entire laboratory. It is the responsibility of the laboratory supervisors to ensure the use of proper laboratory procedures and that thorough quality control measures are in effect at all times. The methodology and internal audit records, precision and accuracy figures are published in Ontario Ministry of the Environment, 1985.

Quality assurance responsibilities are described in the following sections which convey the specific quality control measures prescribed for each sample type under the APIOS project in Dorset. Continuing co-ordination with LSB personnel at both locations in conjunction with the on-going field study provides the basis for quality assurance of data collected in all facets of the project.

4. Experimental Procedures

4.1 Sampling Methodology

Several reports on field methodology have been published to document technical procedures employed in the LCS and APIOS programmes, the most recent being Ministry of the Environment Data Report 83/1 (Scheider et al. 1983a). Although the Data Report Series is intended primarily as a readily available source of basic data, it also includes methodology manuals for field personnel. In addition, a detailed historical record of sampling procedures for each chemical parameter outlining changes to collection handling and analysis will be documented (Locke et al., in prep.).

The sampling routine for the three main types of samples is as follows:

(i) Lakes: A set of six lakes was originally chosen in 1975 as part of the LCS project. This group of lakes was re-evaluated in 1979 with the intent of selecting lakes to quantify the influence of acidic precipitation. Because of the need for a long term data base, overlap in the sets of lakes was maximized. Currently, a set of eight lakes (nine basins) are sampled by-weekly during the ice-free season and monthly during the ice-cover period. In addition to these intensively monitored lakes, other lakes are sampled using the same methodology. A set of eight lakes chosen in 1975 to augment the original LCS lake set is sampled on a monthly basis

(ice-free season only) to provide long-term trends through time. A group of four lakes in Sudbury selected in 1973 as part of of the Sudbury Environmental Study are sampled year-round to monitor long-term trends in water quality. Eleven lakes in Muskoka-Haliburton exhibiting characteristics of stress as a result of acidic deposition are monitored monthly in the ice-free season. A joint study with Ontario Ministry of Natural Resources begun in 1980, encompasses an additional 12 lakes that are sampled monthly during the ice-free season. The sampling methodology for the latter set is outlined by Reid et al. (1984). In addition to the above regularly monitored lakes, each year some lakes are selected to be sampled on a one-time basis. The total number of lakes surveyed in the Muskoka-Haliburton area has grown to about 2000, so that a comprehensive data base now exists.

(ii) Streams: Thirty-two streams are routinely monitored for chemistry and hydrology. These streams were selected in conjunction with the study lakes to investigate the environmental changes that result from acidic precipitation and nutrient inputs. The methods employed in the collection and analysis of chemical and hydrological data are summarized in Scheider et al. (1983a, 1983b).

(iii) Precipitation: A network of seven battery-operated, moisture-activated "wet-only" Kramer samplers and "bulk"

collectors was situated throughout the study area to monitor atmospheric deposition beginning in 1976. Bulk collectors were also set up on rafts on three of the study lakes. Rainfall depth was measured using standard 10-cm diameter polycarbonate precipitation gauges. Nipher gauges were used from November to April to measure snowfall depth. In 1982 the network was reduced to five bulk collectors which were sampled on an event basis. Three additional sites were added in March 1984 and after a suitable period of overlap (to November 1984), four of the five 1982 sites were eliminated, leaving a total of four sites. Precipitation depth is now estimated using Belfort gauges located at each of the four sites. During the winters of 1981/82, 82/83 and 83/84 snow surveys were carried out in three sites in the study area. Plexiglass tubes were used to sample the snow, which was melted then submitted for chemical analysis.

4.2 Quality Control Sampling Schedules

Audits of equipment performance and field sampling procedures are routinely carried out. Intercomparisons with other sampling programmes are also conducted where necessary. Although some QA/QC studies have been carried out continuously since the initiation of the studies in 1975, the studies were expanded in 1983. A comprehensive programme was undertaken in 1983 to document sources of error, including

sample collection and handling, sample analysis and data manipulation. All chemical parameters and field techniques are replicated at routine sampling stations on a rotational basis (Locke et al., in prep.). These procedures are used to isolate sources of error and are outlined in more detail in this section. Detailed statistical analyses of these data will be described in a separate report (Locke, in prep.).

The procedures for the routine QC sampling for each of the three sample types (lakes, streams and precipitation) are as follows:

a) Lakes: Routine chemical sampling of lakes encompasses two techniques. The lake sample is either volume-weighted by depth zone in both stratified and unstratified conditions, or chemical "profiles" are collected by sampling at discrete depth intervals from the surface to the lake bottom. These techniques are outlined by Scheider et al. 1983a).

To estimate variability resulting from sampling equipment and field collection procedures, some samples are replicated (five samples per collection) each week. Each lake is replicated for each parameter group every 16 weeks. One or more of the five replicates are sub-divided into two samples in order to isolate the effects of sample submission procedures and analytical techniques from equipment and field collection effects. The profile samples cannot be sub-divided because they

are stored in gas-tight containers.

b) Streams: Five separate samples (including the regular sample), are obtained weekly from each of four stations and submitted for chemical analysis for one of four parameter groups. The four stations (out of 32) are alternated weekly, as is the parameter group. Each stream is replicated for each parameter group. Beginning in December 1984, selected samples were subdivided and submitted as duplicate samples so that analytical and field variability could be separated.

c) Precipitation: Samples collected at two stations (alternating among the four) were separated into five replicates when sufficient volume was available. These replicates are submitted for chemical analysis of one of four parameter groups on a rotational basis. This allows estimation of the combined field handling and analytical precision. Each precipitation station is replicated for each parameter group once every 9 weeks. To estimate the total precision including that attributable to sampling equipment, field handling and laboratory analysis, two collectors have been used at one of the four sites for the last five years (Locke et al. in prep.).

4.3 Training

Our studies rely on field crews to collect samples using

standardized procedures; therefore, adequate training is of prime importance in meeting the QA/QC objectives. The sample collection and handling procedures of the field crews are audited through regular QA techniques to ensure that the procedures employed are those specified in the technical and operating manual. These routine audits and checks ensure that field personnel are adhering to the standard procedures. Yearly performance reports on all individuals by their supervisors are used to verify that proper methodology is being used.

Precision and accuracy of the analytical work is the responsibility of the LSB personnel. Methodology for all analysis is outlined in Ontario Ministry of the Environment, 1983.

5. Equipment and Materials

5.1 Instrumentation

Equipment is calibrated, installed, used and maintained by following uniform guidelines that were developed at the outset of the study (Scheider *et al.* 1983a; Locke *et al.* in prep.). Routine calibrations and preventative maintenance procedures are documented, and these records are kept for historical reference. An inventory of all equipment used, supplies and spare parts is also kept up to date. Periodically, equipment is replaced and/or procedures for operation are altered. Intercomparison measurements are used to ensure that results are consistent. The results of these inter-

comparisons, along with the rationale for changing methodology and/or equipment is kept on file. The use and maintenance of equipment forms a major part of the field technicians' responsibilities and the necessity for intensive training, detailed documentation of sampling procedures, and periodic performance audits is vital to the achievement of the QA/QC objectives.

5.2 Sample Handling

Sample bottles obtained from central stores of the LSB are frequently tested for contamination by preparing "blanks". Similarly, the sampling equipment (e.g. precipitation collectors, lake water collectors, etc.) is continually monitored for contaminants. Blanks (de-ionized water stored in these collectors for varying lengths of time) are submitted for chemical analysis. These data are utilized in conjunction with the data obtained for replicate samples (Section 4.2) to assess the sources of variability.

The requirements for sample preservation during transit and prior to analysis (temperature, filtration, sealing and chemical fixing agents) are documented in Scheider *et al.* (1983a) and Locke *et al.* (in prep.). Additionally, comprehensive information for each sampling event including specific sample identification is recorded in field books, which are permanently stored on site for reference. Complete sample submission summaries are also kept for all samples.

5.3 Special Studies

In addition to the regular long-term limnological programmes, many other short-term scientific studies are conducted at the Dorset Research Centre. QA/QC procedures for these studies are the responsibility of the project scientists, but are necessarily consistent with the QA/QC programme.

6. Sample Analysis

Samples collected at Dorset are sent to three laboratories for sample analysis: the WQS in Dorset and Rexdale, and the ITC Laboratory in Rexdale. Records of the location of all sample analyses and analytical techniques employed are maintained by LSB staff. This documentation (Ontario Ministry of the Environment, 1985) includes a description of the methods or techniques, the precision and accurancy of each technique and operating and calibration procedures.

The WQS in Dorset handles all perishable parameters while the central laboratory in Rexdale analyzes all other chemical parameters. The WQS and ITC publish yearly quality control reports which are made available for reference (Ontario Ministry of the Environment, 1985). Analytical equipment in both Dorset and Rexdale is calibrated regularly using prescribed calibration reference standards. Control standards are used to detect deterioration in instrumentation, chemicals or handling technique and these observations are readily available.

Because the perishability of samples is a major concern, the priority of chemical analysis is established based on sample stability.

7. Data Management

7.1 Data Storage and Retrieval

All data collected as part of the Dorset programmes are stored in computer files. Chemical analyses from the central laboratory are processed by the Laboratory Information System (LIS). LIS personnel enter the sample submission numbers and field data information, and these data are later paired with the chemical analyses in the LIS. The chemistry data are checked by senior staff in the central chemistry laboratory prior to approval on the LIS. The LIS makes weekly data transfers of approved submission sets to the Downsview computer centre where it is used to update the Sample Information System (SIS) data base. The chemical data collected at the WQS chemistry laboratory in Dorset are entered and verified directly on the Hewlett-Packard desk-top computer. They are periodically transferred to the Downsview computer centre and used to update the SIS data base. Periodically, LIS Station Detail Report with each submission's chemical and physical data are generated and sent to the Dorset laboratory prior to our data editing procedures. The data are retrieved from SIS onto nine-track tapes, and the data files transferred to the Hewlett-Packard 9845B desk-top computers. The

above procedures for data entry storage and retrieval are well-documented and a user manual is available for all field personnel (Ontario Ministry of the Environment, 1984b). The manual includes information for both sample submission coding and request for chemical analysis to the central laboratory.

The quality control data are entered in the computer files in the same manner as the Dorset lab results. These data are subject to the same accuracy checks and editing processes. The results of these procedures are contained in detail in a separate report (Locke, in prep.).

7.2 Data Evaluation

All chemical data are processed by a data editing programme ("EDIT") that assists in identifying errors and inconsistencies (Locke *et al.* in prep.). The determination of which data are valid is based principally on the results of this programme, but other factors including sample chemistry and sample history are taken into account. The routine quality control data, as well as the chemical methodology record provide a valuable reference tool. Each station is reviewed individually, and in association with other influencing factors such as weather and hydrologic flow conditions, the data are assessed for accuracy, precision and representativeness.

An additional part of the data editing procedure includes station-specific analysis for each parameter as a function of

time. These trend-through-time data provide a valuable interpretive tool for the data evaluation process.

7.3 Data Reporting

It is the responsibility of project scientists to report the results of their studies either as publications in the scientific literature or as MOE reports. The frequency of data reporting is in accordance with requirements to keep senior management and the scientific community informed of any new and important findings. Release of unpublished data is limited to special requests and is closely monitored. Publication must include peer review of all reports and papers, and the appropriate internal approvals.

8. References

Mills, J.S. 1985. Acid Precipitation in Ontario Study. Quality Management Plan. LCS and QA Section, LSB M.O.E., Rexdale.

Ontario Ministry of the Environment. 1983. Handbook of Analytical Methods for Environmental Samples. Laboratory Services and Applied Research Branch.

Ontario Ministry of the Environment. 1984a. Quality Assurance Plan. APIOS Deposition Monitoring Program. ARB-76-84-ARSP, Air Resources Branch, Atmospheric Research and Special Programs Section, Internal Report.

Ontario Ministry of the Environment. 1984b. User Manual for the Lab Information System (LIS). Limnology Unit, Water Resources Branch, Internal Report.

Ontario Ministry of the Environment. 1985. 1982-1984 Performance Report. Ontario Ministry of the Environment, Laboratory Services Branch, Water Quality Section, D85001.

Reid, R.A., B.A. Locke, R.E. Girard and A.C. Nicolls. 1984. Physical and Chemical Data Summary for Twelve Selected Lakes in the Muskoka-Haliburton Area (1981-1983). M.O.E. Data Report DR 84/1.

Scheider, W.A., R.A. Reid, B.A. Locke and L.D. Scott. 1983a. Studies of lakes and watersheds in Muskoka-Haliburton, Ontario: Methodology (1976-1982). Ontario Ministry of the Environment Data Report DR 83/1.

Scheider, W.A., C.M. Cox and L.D. Scott. 1983b. Hydrological Data for Lakes and Watersheds in the Muskoka--Haliburton Study Area (1976-1980) M.O.E. Data Report DR 83/6.